Effect of Trapped Ions in a Gated Time-of-Flight Apparatus

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ABSTRACT

A three-mesh gate is used in a time-of-flight (TOF) apparatus to analyze the velocity of positive ions. Test results and a theoretical description are presented of an effect arising from trapping ions between meshes of a two gate TOF velocity analyzer. The entrapped ions produce a side peak in the TOF spectra corresponding to faster ions. The onset and relative height of the side peak is dependent on the gating voltage and risetime of the pulsing electronics, while the relative intensity depends upon the velocity being sampled and the ratio of the gate width to duration.

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1. Introduction

The time-of-flight (TOF) mass spectrometer has been increasingly used for measurements of various ionization process including electron-impact [1,2], laser ionization involving surface [3] and resonance-enhanced multiphoton ionization techniques [4,5]. The advantages of TOF methods lie in their ability to measure velocity distributions; and entire mass spectra in a single cycle. However, the resolution of a TOFMS depends on flight time and the initial energy distribution of the ions. Various techniques are used to reduce the initial energy distribution of the ions, such as supersonic jet sources [2] and ion reflecting mirrors [3,6,7] .

Timing techniques involving a pulsed-mesh have regained popularity with the availability of fast, high voltage square-pulse generators based on the power metal-oxide-semiconductor field effect transistor (pMOSFET) [8]. The use of pulsed-meshes has led to various experimental artifacts involving, for example, the risetime of the pulsing electronics in electron-impact TOF mass spectrometers [2], and the gate duration time t_g on ion transit-time measurements using the four-mesh TOF technique [9].

In the present study a gated TOF apparatus [10] is used to determine velocity distributions of ions by measuring the flight time between two pulsed gates a known distance L apart. A schematic diagram is shown in Fig. 1. The first gate, at the entrance of the field free flight region, opens momentarily letting a packet of ions enter the TOF tube. The ion packet separates according to velocity where the faster ions reach the exit gate before the slower ions. Ions of a particular velocity can be selected by opening the second gate after a suitable time delay. Each gate consists of three meshes. The two outer meshes are grounded to shield the flight region from the pulsing voltage on the center mesh. The center mesh repels ions when biased positively and opens momentarily by switching to ground.

The present work investigates the effect of a finite gate width and a time dependent electric field within the present three-mesh gate geometry. It was found that when the gate closed the ions in the gate structure were accelerated by the pulsing electronics, thus modifying the velocity distribution being measured. The accelerated ions form a faster side peak in the TOF spectra. This peak is characterized by its TOF and relative height. Sec. 2 outlines the experimental apparatus used in the present measurements. The theory and numerical calculation used to model the experimental results are given in Sec. 3 and a discussion of the results are presented in Sec. 4.

II. Experimental Method

The three-mesh pulsed gate TOF apparatus has been described in detail in a previous paper [9] and is briefly described here with an emphasis on the pertinent details. The experimental apparatus consists of three parts: the ion source, the time-of-flight tube, and the lens and detection system.

The ion source is a commercial ionizer (Extrel, Inc.) with an effusive gas inlet. Ions are extracted from the ionization region with an energy distribution that depends on the space-charge potential variation of the ionizing electron beam, and on penetration of the extraction voltage into the source region. The chamber pressure during operation is of the order 1×10^{-8} Torr with a background of 4×10^{-9} Torr. Ultra-high purity (99.999%) argon is used as a target gas and impurities in the gas line are removed by freezing with liquid N_2.

The field free flight region of the TOF tube is defined by the distance L between the center meshes in the gates G_1 and G_2 at the entrance and exit of the flight tube (Fig. 1). In the present application L = 18.0 cm. The gates consist of three 95%-transmitting tungsten meshes in series separated by a distance d = 1.5 mm. The center mesh is held at a potential

V_g reflecting ions with energy less than qV_g. The voltages applied to the center mesh can be varied from O to + 200 V. The two outer meshes are grounded to terminate the field generated by the potential applied to the center mesh.

The ion lens system, detection system, and the three-gate controlling electronics have been described previously [10]. The electronics arc modified in the present work to pulse only the first and third gates of the three-gate system. The pulsed element of the middle gate (not illustrated in Fig. 1) is grounded, thereby eliminating its effect on the ion trajectories. The system is operated in a low duty cycle mode (2%) where alias velocity peaks are eliminated [1 O]. The gates are pulsed at a frequency of 22 kHz with a pulse width of 1.0 µsec. The flight times measured ranged from 0.0 to 20.0 µsec. The data acquisition is controlled by a multichannel analyzer where typical dwell times in each channel range from 0.1 to 5.0 sec.

111. Model of Accelerated Ions

The goal of the model is to quantify the effects of a spatially finite gate and a non-zero risetime of the pulsing electronics. The major aspects of the entrapped spectra are the relative intensity and location of the leading edge of the side peak. The spectra are modelled by first assuming a Maxwell-Boltzmann velocity distribution

$$F(v)dv = 4\pi n\left(\frac{m}{2\pi kT_i}\right)^{\frac{3}{2}} v^2 e^{-mv^2/2kT_i} dv, \tag{1}$$

where n is the number of ions, m the mass of the ion, T_i the ion temperature, k is the Boltzmann constant, and v the ion velocity. A flight-time distribution D(t) is obtained by transforming the velocity distribution function F(v) from velocity to time domain [11]

$$D(t)dt = \frac{L}{t^2} F\left(\frac{L}{t}\right) dt$$

$$= 4\pi n \left[\frac{m}{2\pi k T_i}\right]^{\frac{3}{2}} \frac{L^3}{t^4} e^{-mL^2/2kT_i t^2} dt, \quad (2)$$

where L is the length of the flight tube. The TOF spectrum I(t) is calculated by convoluting Eq. (2) with the transmission function of the gates. The transmission function for an ideal gate, $t_g = 0$ and $d = 0$, is a delta function. If one gate opens for a period t_g while the other opens momentarily the resulting transmission function is rectangular with a base width of t_g. If the gate duration of both gates is t_g the transmission function is triangular with a base width of $2t_g$.

Due to the risetime of the electric field and the finite width of the gate the flight-time distribution is perturbed for the ions entrapped in the gate. Ions caught between the pulsed-mesh and the grounded mesh are accelerated when the gate closes. The final ion energy depends on the position of the ion in the gate, the pulsing voltage, and the risetime of the pulsing electric field. The time dependence of the electric field is given by

$$E(t) = E_o\left[1 - e^{-t/\tau}\right]^2, \quad (3)$$

where E. is the applied electric field and τ is the I/e risetime of the exponential. The risetime for the electric field to increase in magnitude from 0.1 E_o to 0.9 E_o is just 2.59 τ. The functional form of Eq. (3) for the electric field describes the present pulse shape as measured on a fast oscilloscope and is the same form as that used in Ref. 2. The effect of the fall-time of the electric field on the flight times is negligible since the ions are repelled by the gate.

The overall flight time T of the ions trapped by the gate the ion flight time is given by

$$T = t_1 + t_2 + t_3, \tag{4}$$

where t_1 is the field-free time of the ion in the open gate G_1, t_2 is the time required for the ion to exit the gate while being accelerated by the pulsed electric field, and t_3 is the remaining time in the flight tube. The distance x_0 the ion travels before the gate closes is related to t_1 by

$$x_0 = v_0 t_1, \tag{5}$$

where V. is the initial ion velocity. It should be noted that if X. is greater than twice the distance d between the pulsed and grounded mesh, the total ion flight time is unaffected by the acceleration and is given by L/v_0. For $d < x_0 < 2d$, the ion experiences a force given by

$$F(t) = m\frac{dv}{dt} = qE(t) = \frac{qV_g}{d}\left[1 - e^{-t/\tau}\right]^2, \tag{6}$$

where V_g is the potential applied to the center mesh and v is the ion velocity. Integrating Eq. (6) between the initial and final velocity at times t‘ = O and t respectively yields

$$\begin{aligned} v - v_o &= \int_0^t \frac{qV_g}{md}\left[1 - e^{-t'/\tau}\right]^2 dt' \\ &= -\frac{qV_g}{md}\left[\frac{3}{2}\tau - t - 2\tau e^{-t/\tau} + \frac{\tau}{2}e^{-2t/\tau}\right]. \end{aligned} \tag{7}$$

Integrating Eq. (7) between the initial X. and final position 2d of the ion at times t’ = O and t, respectively; results in the position of the ion as a function of time given by

$$\begin{aligned} 2d - x_o &= \int_0^t v_o dt' - \frac{qV_g}{md}\int_0^t \left[\frac{3}{2}\tau - t' - 2\tau e^{-t'/\tau} + \frac{\tau}{2}e^{-2t'/\tau}\right]dt' \\ &= v_o t + \frac{qV_g}{md}\left[\frac{7}{4}\tau^2 - \frac{3}{2}\tau t + \frac{t^2}{2} - 2\tau^2 e^{-t/\tau} + \frac{\tau^2}{4}e^{-2t/\tau}\right], \end{aligned} \tag{8}$$

where x_0 is the position of the ion when the gate closes (t' = O). For each value of 2d - x_0 Eq. (8) can be solved iteratively to obtain $t \equiv t2$. The time t2 is then used to calculate the ion exit velocity v using Eq. (7). This velocity, in turn, yields the time in the tube, $t_3=(L-d)/v$ (see Fig. 1). Note, for an ideal pulse ($\tau=0$) the velocity and position [Eqs. (7) and (8)] reduce to the standard equation of motion of a particle in a time independent electric field.

The TOF spectrum is given by the convolution of the transmission function of the two gates G_1 and G_2, and the flight time distribution D(t) [Eq. (2)]. For convenience in calculating the convolutions, D(t) and the gate transmission functions were divided into sufficiently narrow bins. Hence the convolution of the flight-time distribution and the transmission function of each gate are treated as sums over binned distributions. The distribution D(t) is divided into i time bins ranging in time from t_1 to t_i. The distribution is truncated at the i^{th} bin having an amplitude less than 10^{-6} the peak value.

The gate width t_g of G_1 is divided into j time bins each of 1 nsec width, and G_2 into k bins also of 1 nsec width. A time element i in D(t) can be found in any bin j in G_1. In addition, an ion present in any of the j bins of G_1 can be transmitted through to k bins in G_2 subject to the relevant flight-time constrains.

The ion position is calculated at time t_g for the i^{th} element of D(t) in the j^{th} bin of G_1. If the ion position is outside the gate (x. > 2d) the flight time is t_i. However, if the ion is located within the gate the flight time is given by Eq. (4) where t_1, t_2, and t_3 are calculated using the above prescription.

The final TOF spectral intensity I(t) can then be expressed as

$$I(t) = \sum_i \sum_j \sum_k D(i,j,k). \qquad (9)$$

The time ranges in Eq. (9) arc $i\{t_1, t_i\}$, $j\{0, t_g\}$, and $k\{T + t_j - t_g, T + t_j)$ where t_j is the time corresponding to the j^{th} bin in G_1. The last interval follows from the fact that the width t_g of G_2 is convoluted with the width of G_1 so that the time window is extended.

IV. Results and Discussion

Figure 2 is the TOF spectrum resulting from the electron impact ionization of argon accelerated to an energy of 30 eV with the background signal subtracted out. The background spectra is obtained by scanning the flight time of the residual gas in the chamber without a target gas present. The spectra show the main feature at 15.1 µsec corresponding to 30.0 eV argon ions traveling with a velocity of 1.20 x 10^6 cm/see, and a weaker peak to the left. The width of the main peak is related to the ion energy distribution in the source via Eq. (1). The less intense feature is characterized by its relative height and the position of either its onset or maximum. In the present work the *onset* is used to compare the theoretical model with the experimental results. It is observed at 7.2 ± 0.3 µsec having a relative intensity of approximately 4% of the main feature. The weaker side structure in Fig. 2 is expanded by a factor of five to enhance the comparison between the experiment and theory.

The solid line in Fig. 2 represents the model calculation using a Maxwell-Boltzmann distribution [Eq. (1)] with a peak velocity of 1.2 x 10^6 cm/sec and an effective source temperature of T_i = 200 K. The gating voltage and risetime in this spectrum and in the model calculation is V_g = + 130 V and τ = 0.0275 µsec, respectively, As can be seen at the wings of the main peak the fit of the velocity distribution suggests that the source of the ions does not precisely conform to a standard Maxwell-Boltzmann distribution of speeds. The energy distribution of the source, in this case, is not a function of source temperature alone but also of potential variations due to the space charge of the electron beam and the extraction field.

It is apparent from Eqs. (7) and (8) that the onset is related to the V_g. Figure 3 illustrates the variation of the onset time as a function of gate voltage. The results of the model onsets in Fig. 3 are extended below the lowest measured gate voltage (40 V) to illustrate the trend of data.

The relative height of the side peak depends on the ratio of trapped ions to the total number of ions. As the pulse width of the gate increases this ratio decreases, hence the relative height of the side peak decreases. It should be noted that the total number of trapped ions does not depend on the gate voltage, so that the area of the side peak is a constant. However, the entrapment has a greater effect on slower velocity distributions since the relative fraction of ions passing through the gate before the gate closes is greater for the faster ions than the slower ions.

In Ref. 10a three-gate TOF apparatus is used to measure velocity distributions. A higher duty cycle, without degradation of the spectra by alias velocities, is achieved by employing the three-gate system. Further alterations to the shoulder by the exit gate or second gate in a three-gate system are neglected. The third gate defines the time interval and any change in the ion energy after exiting the flight tube has no bearing on the time measurement. The center gate, in a three-gate system, would introduce an additional effect of increasing the intensity of the side peak. However, an additional gate would not alter the spectra other than by increasing the background signal. The energy of the ions once ‘accelerated are comparable to the gate voltage and any additional energy the ion acquires reduces the effectiveness of the gating structure.

It has been demonstrated that the pulsed-mesh TOF velocity analyzer accurately measures flight time distributions of low energy ions and that the flight time distributions are perturbed by ions trapped in the gating structure. The resulting spectra include a side peak characterized by its intensity and onset (or maximum). The effect has been successfully modelled by including a time-dependent electric field, spatially finite gate, and temporally finite gate pulsing in the calculation of the flight times.

The acceleration of the ions is an unavoidable effect of pulsed-mesh structures and must be addressed either theoretically or experimentally. In this paper the theoretical approach to model the trapped ions is investigated. An experimental method to reduce the effect employs a “defocusing” method by introducing an electric field having components perpendicular to the flight path. (This can, be done using a course center mesh giving rise to a “bumpy” electric field at the mesh surface.) The trapped ions between meshes are then accelerated off the flight path axis and eliminated from the spectra.

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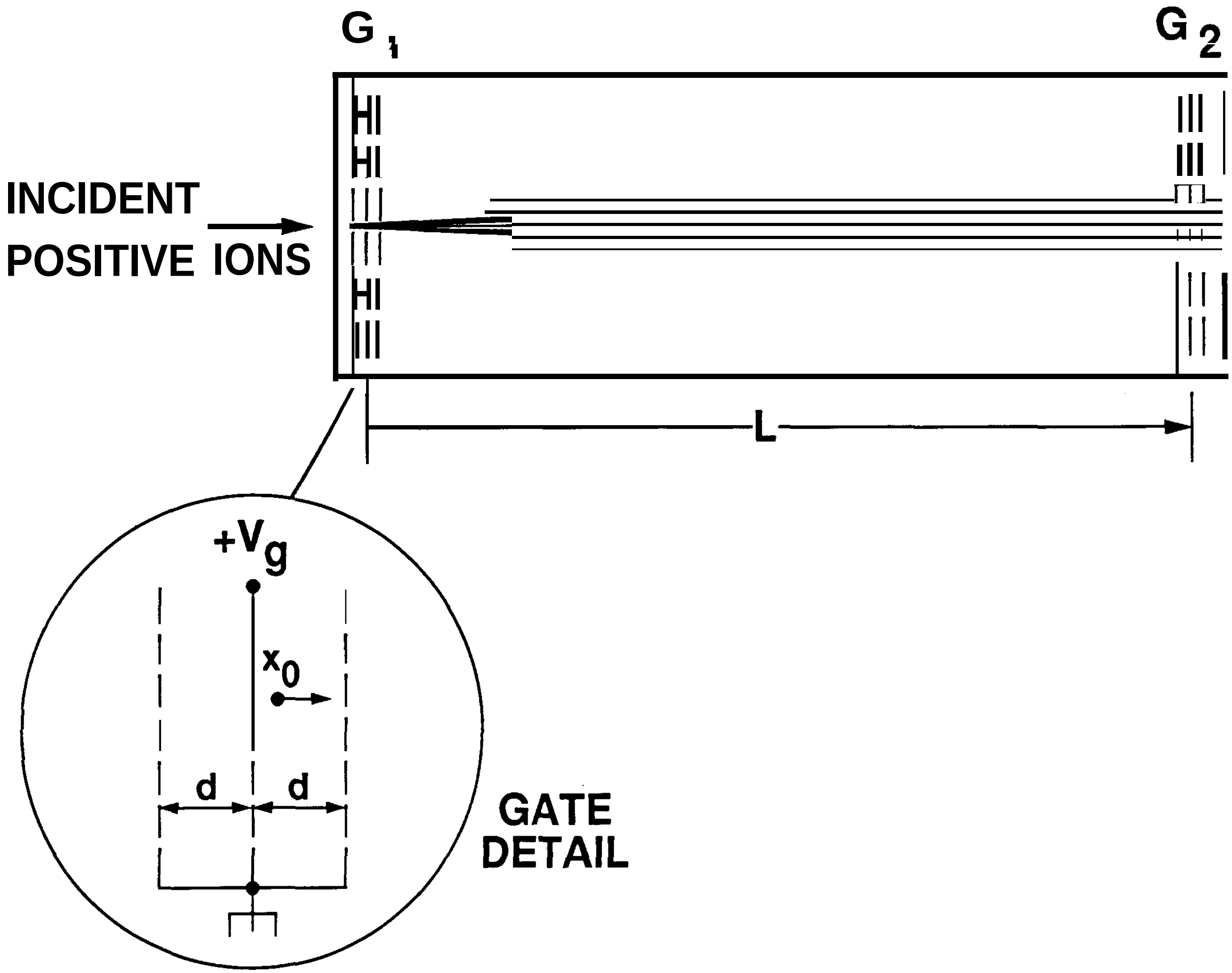
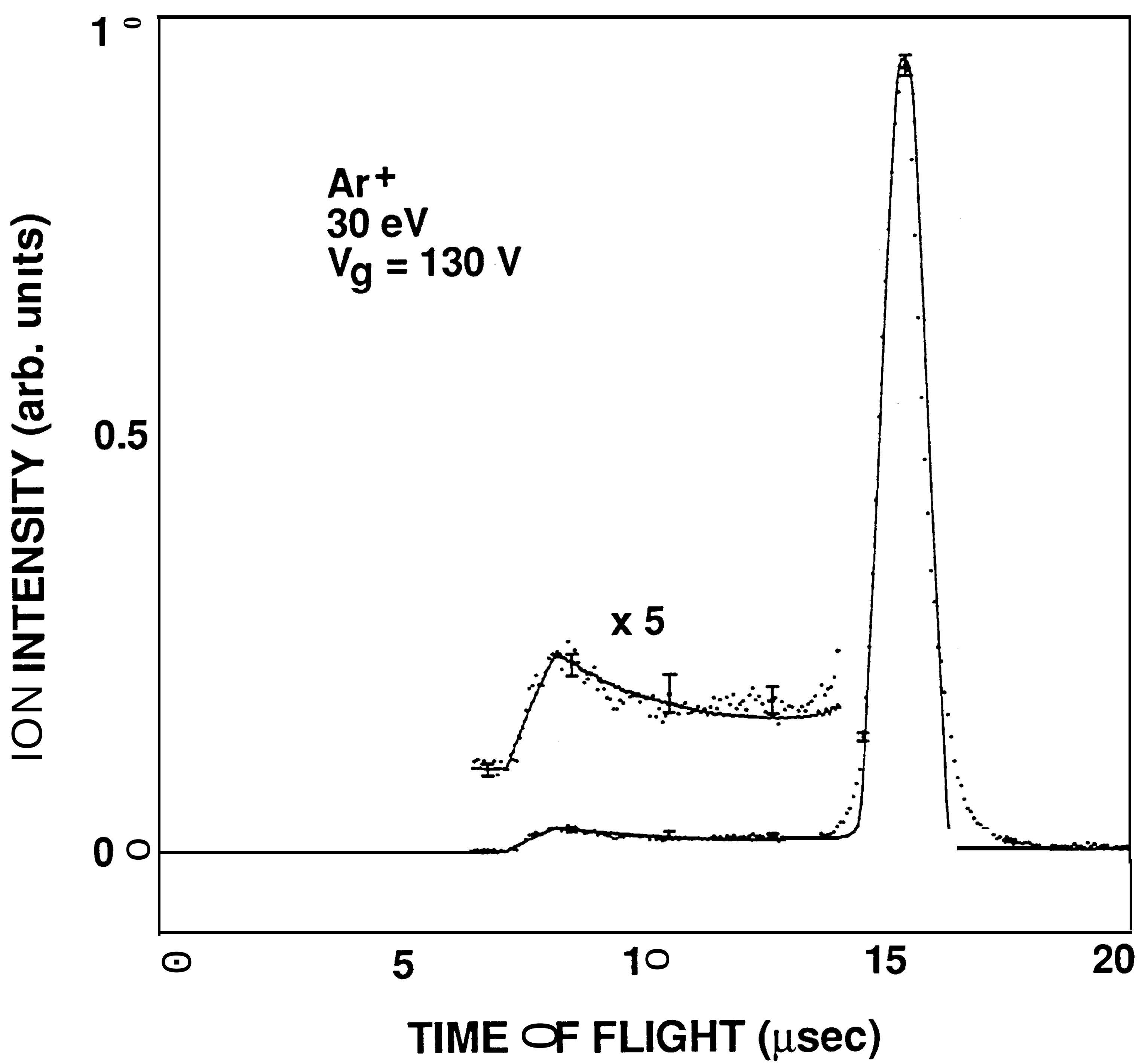
FIGURE CAPTIONS

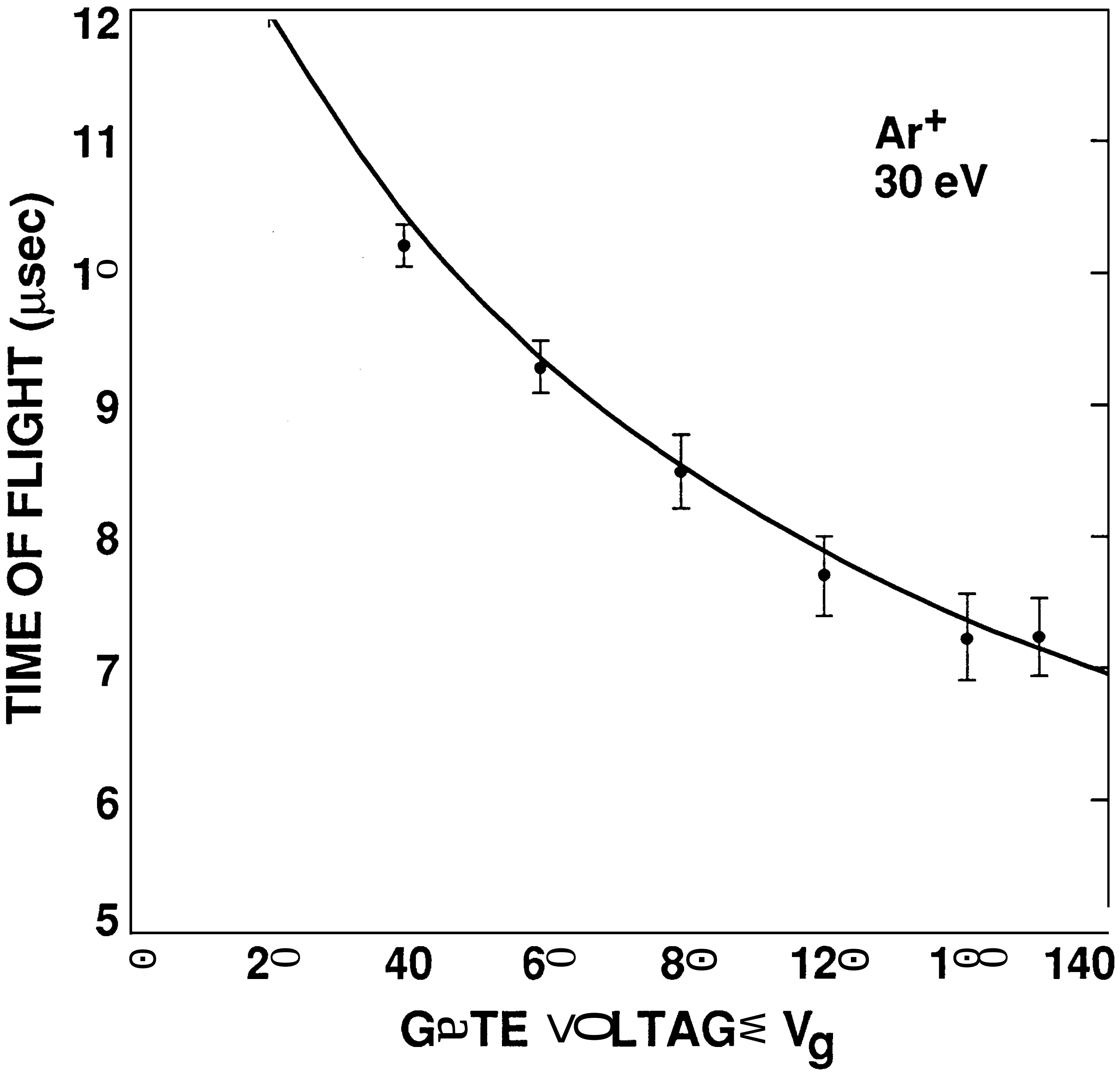
Figure 1. Diagram (not to scale) of the time-of-flight region and gate structures. The length of the flight region, L, is defined by the center mesh of each gate structure. The outer meshes of each gate are held at ground potential and are spaced a distance d from the pulsed center mesh. The position x_0 illustrates one ion location when the gate closes. Distances used herein are L = 18.0 cm and d = 0.15 cm. Shown in the figure are sample trajectories in the flight tube.

Figure 2. Time-of-flight spectrum demonstrating the side peak arising from the trapped ions. The experimental results and associated statistical error bars are shown along with the model spectrum (solid line) derived from a Maxwell-Boltzmann velocity distribution. The shoulder is expanded by a factor of five to enhance the comparison between experiment and model,

Figure 3. Variation of the onset flight time as a function of gate voltage V_g. The filled circles represent the experimental results and the solid line is the result of the modelling.


G 1
G 2
INCIDENT POSITIVE IONS
L
+Vg
x0
d
d
GATE DETAIL


Ar+
30 eV
V_g = 130 V
x 5
ION INTENSITY (arb. units)
TIME OF FLIGHT (μsec)
1.0
0.5
0.0
0
5
10
15
20



Ar+
30 eV
TIME OF FLIGHT (μsec)
GATE VOLTAGE V_g